Metal-Ion-Retention Properties of the Poly(2-acrylamido-2-methyl-1-propanosulfonic acid-*co*-4-vinyl pyridine) Resin

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ABSTRACT: The water-insoluble resin poly(2-acrylamido-2-methyl-1-propanosulfonic acid-*co*-4-vinyl pyridine), through a radical polymerization solution, was synthesized with ammonium persulfate as an initiator and *N,N*-methylene bisacrylamide as a crosslinking reagent. The metal-ion-retention properties were studied by batch and column equilibrium procedures for the following metal ions: Hg(II), Cu(II), Cd(II), Zn(II), Pb(II), and Cr(III). These properties were investigated under competitive and noncompetitive conditions. The effects of the pH, maximum retention capacity, and regeneration capacity were studied. The resin showed a high retention ability for Hg(II) ions at pH 2.0. The

retention of Hg(II) ions from a mixture of ions was greater than 90%. The resin showed a high selectivity for Hg(II) with respect to other metal ions. The Hg(II)-loaded resin was able to be recovered with 4M HClO$_4$. The retention capacity was kept after four cycles of adsorption and desorption. The retention properties for Hg(II) were very similar with the batch and column methods. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 90: 3556–3562, 2003

Key words: synthesis; metal–polymer complexes; ion exchangers; resins

INTRODUCTION

Polymeric materials containing chelating groups that adsorb metal ions are applied to solving a variety of ecological and industrial waste problems.[1–4] Therefore, such polymers continue to attract the attention of many researchers.[5–25] The design of tailored chelating agents represents one of the basic challenges in the field of synthetic coordination chemistry. Tailored chelators can be used to govern the stability of a complex or to modulate the electronic properties of a metal cation. Chelate-forming polymeric ligands characterized by reactive functional groups containing O, N, P, S, and donor atoms and capable of coordinating different metal ions have been extensively studied.[16–25] The materials most often show preferential selectivity toward certain metal ions, and this facilitates their use for the preconcentration and separation of trace metal ions from saline and nonsaline waters.

Ion-exchange resins are very important to metal-ion complexation reactions because of their hydrophilicity, accessibility, and high capacity, but the synthesis of a polymer with a greater degree of selectivity could be important to different applications. However, because of the wide range of materials and methods of synthesis, it

is not surprising that a chelating exchanger's physical form may vary from a rock-hard material to a soft gel. The desirable properties of chelating exchangers are fourfold: (1) a high capacity for the metal(s) of interest, (2) high selectivity, (3) fast kinetics and rapid equilibration with metal-containing solutions, and (4) high mechanical strength and toughness of the exchanger particles. Unfortunately, the last two are competitive.

This article reports the metal-ion-retention properties of the resin poly(2-acrylamido-2-methyl-1-propanosulfonic acid-*co*-4-vinyl pyridine) [P(APSA-*co*-4-VPy)] with batch and column equilibrium procedures. The metal ions were selected according to their environmental impact.

EXPERIMENTAL

Reagents

4-Vinylpyridine (4-VPy; Aldrich, Milwaukee, WI) was purified by distillation. 2-Acrylamido-2-methyl-1-propanosulfonic acid (APSA; Merck, Stuttgart, Germany), ammonium persulfate (APS; Merck), and *N,N*-methylene bisacrylamide (MBA; Merck) were used as received.

Trihydrated copper nitrate, tetrahydrated cadmium nitrate, mercury nitrate, hexahydrated zinc nitrate, lead nitrate, and nonahydrated chromium nitrate (Merck) were analytical-grade; perchloric acid (Merck), nitric acid (Merck), and sodium hydroxide (Merck) were used.

Synthesis of the adsorbents

The synthesis of the P(APSA-*co*-4-VPy) resin was carried out with a radical initiator. To a polymerization
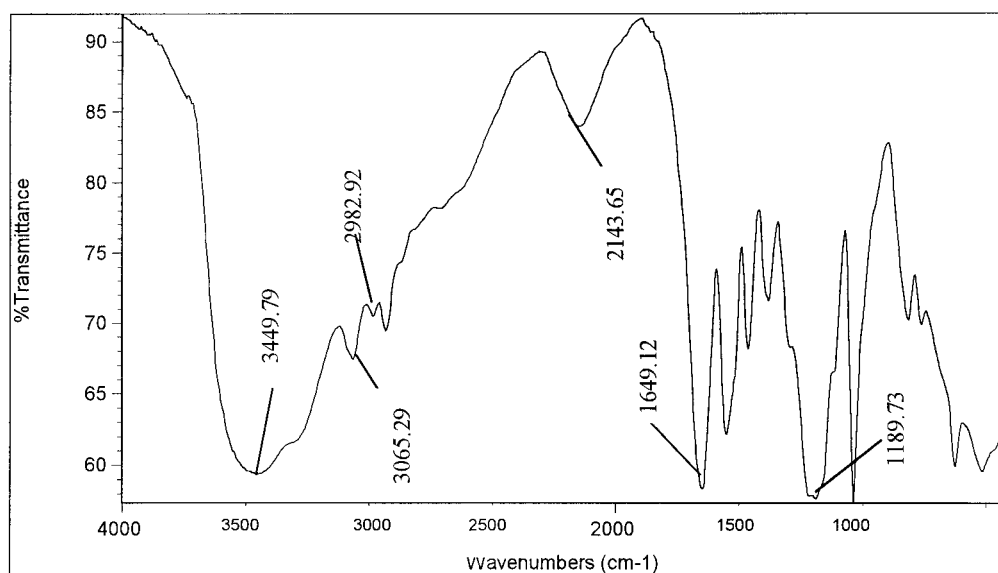
Figure 1 FTIR spectrum of the P(APSA-*co*-4VPy) resin.

flask, the two monomers APSA (0.05 mol) and 4-VPy (0.05 mol), the crosslinking reagent *N,N'*-methylene bisacrylamide (2×10^{-3} mol), and the initiator APS (0.5 mol %; 5×10^{-4} mol) were added. The system was kept under N_2 for 3 h at 70°C. Subsequently, the resin was filtered and washed with abundant distilled water and dried *in vacuo* at 50°C until a constant weight was obtained. This synthesis was performed with the amount of crosslinking ranging from 2 to 8 mol %. The dried resin was ground, and a particle size of 180–250 μm was used in all the experiments.

The copolymer composition was determined by elemental analysis, with consideration given to an analysis of sulfur coming from the APSA comonomer, which was not present in the 4-VPy comonomer.

Sorption equilibrium procedure

A batch-type equilibrium procedure was employed in all the sorption runs. The sorption equilibrium exper-

iments were used to study the effects of the pH values on the sorption, the determination of the maximum binding capacity, and the selectivity sorption from mixtures of metal ions.

Dried samples (50 mg each) of the chelating resin were equilibrated for 1 h in 5-mL metal-ion solutions at 20°C. The different metal-ion aqueous solutions were adjusted to the desired pH values with nitric acid or sodium hydroxide before equilibrium. The loaded sample resins were filtered and washed with distilled water. The concentrations of metal ions in the filtrate were determined by atomic absorption spectroscopy. Batch metal uptake experiments under competitive conditions were also carried out. The following metal-ion mixture was made: 0.1-g batches of the resin were added to a mixture of 10 mL (4.4×10^{-4} *M*) of each metal ion
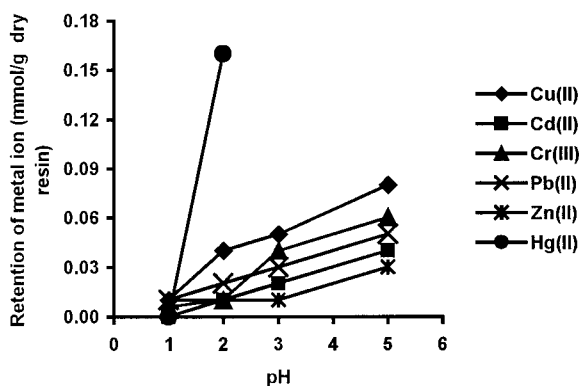

Figure 2 Effect of the pH on the metal-ion retention (mmol of metal ion/of g dry resin) of the P(APSA-*co*-4VPy) resin (batch equilibrium procedure).
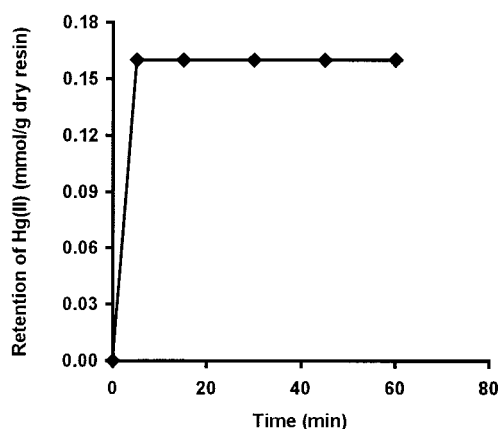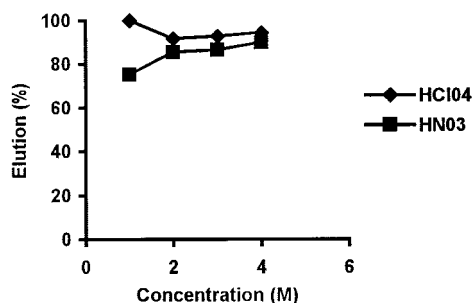

Figure 3 Retention (%) of Hg(II) at pH 2.0 at different times (min). The initial concentration of Hg(II) was 0.16 mmol/g of dry resin (batch equilibrium procedure).

Figure 4 Elution behavior of the loaded resin with mercury ions with $HClO_4$ and HNO_3 at different concentrations.

[Cu(II), Hg(II), Cd(II), Zn(II), Pb(II), and Cr(III)]. After being shaken for 1 h, the samples were further handled as described previously for noncompetitive conditions. So that the maximum sorption capacity for Hg(II) ions would be obtained, 50 mL of an aqueous solution (5.2×10^{-3} M) was shaken with 1 g of the dry resin for 1 h at 20°C. The mixture in the flask was filtered, washed with distilled water, and transferred into a calibrated flask. The process was repeated three times, the volume was increased to 250 mL, and the metals were determined by atomic absorption spectroscopy.

In competitive sorption studies, solutions containing all ions were used.

In the column experiments, 0.2 g of the resin was placed in a column 15 cm long and 1 cm in diameter. This column was used with only 0.2 g of the resin to ensure adequate metal-ion-retention behavior during all the preliminary experiments. For the packing of the resin, water at the same pH was used. In all, a 20-mL

metal salt solution passed through the column. The fractions were collected and analyzed for the metal-ion concentration.

Removal of the mercury(II) ions

The loaded resin with mercury(II) (0.1 g) was stirred with $HClO_4$ and HNO_3 (10 mL, 1–4M). The desorbed metal ions were collected and estimated as previously described.

Measurements

A Julabo air-batch shaker (Germany) was used for shaking the solution at a desired temperature. The pH was measured with a Jurgens digital pH meter (Germany). A Unicam Solar M series atomic absorption spectrometer (UK) was used for the determination of single and mixed metal ions. The Fourier transform infrared (FTIR) spectra of the samples were recorded with a Magna Nicolet 550 spectrophotometer (USA). The thermograms of the loaded and unloaded resins were recorded on an STA-625 thermoanalyzer (Polymer Laboratories, UK). Approximately 5 mg of the dry sample was heated at 10°C/min under a dynamic nitrogen atmosphere.

RESULTS AND DISCUSSION

The water-insoluble resin P(APS-co-4-VPy), through a radical polymerization solution, was synthesized with APS as an initiator and MBA as a crosslinking reagent. The general polymerization reaction can be schematized as follows:
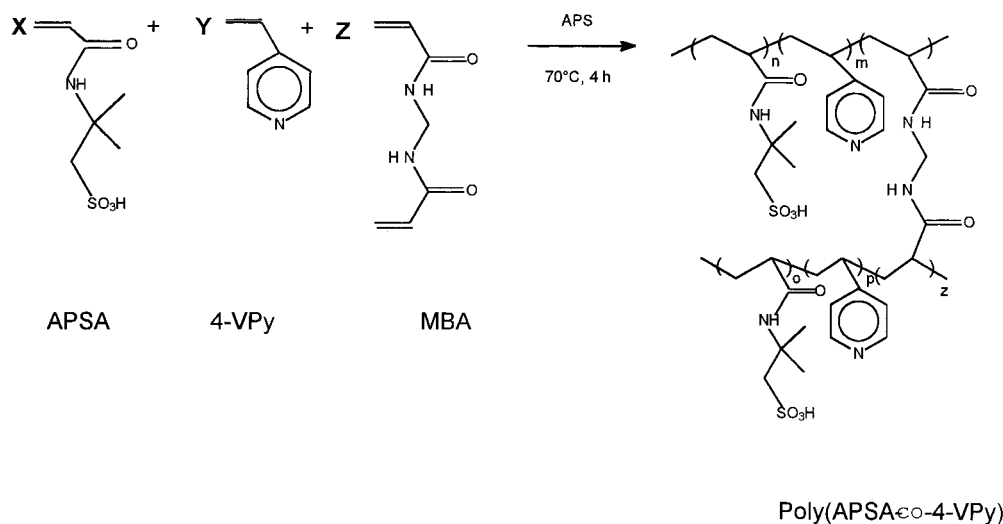
The resin is a nonporous material. The yield is very high, varying from 97.6 to 98.6%, about 60% of it

having a particle size greater than 500 μm; however, it does not depend on the crosslinking ratio.
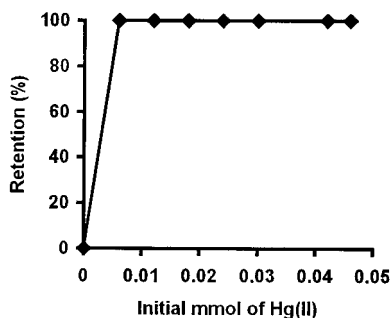
Figure 5 Retention (%) versus the initial amount of the Hg(II) ions (mmol; column equilibrium procedure).

Figure 7 Figura 7 Retention (%) of Hg(II) ions at different contact times (column equilibrium procedure).
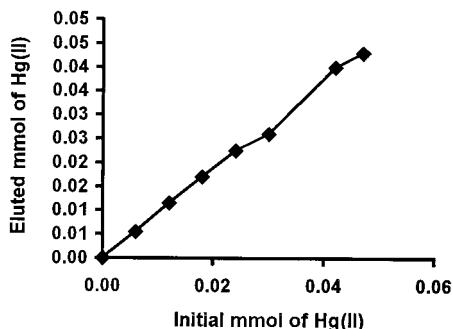
The resin also shows a high thermal stability up to 200°C with a weight loss of lower than 10%. At 300°C, the weight loss is 30%. It can be attributed to the higher stability of the pyridine ring.

An FTIR spectrum of the P(APSA-*co*-4-VPy) resin shows among the absorption bands the most characteristic ones (cm^{-1}): 625.3 (weak; C—S stretching), 1189.7 (strong; S═O stretching), 1649.1 (C═O stretching of a secondary amide), 2143.6 (pyridine), 2931.7 (C—H aliphatic stretching), 3065.2 (═C—H aromatic), and 3449.7 (variable; N—H stretching of a secondary amide; see Fig. 1).
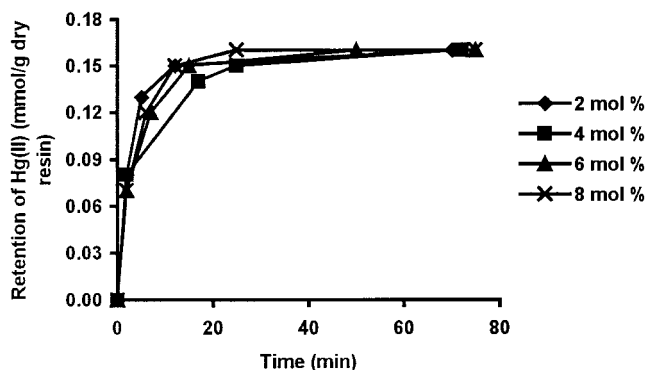
The copolymer composition was determined by a comparison of the intensities of the characteristic absorption signals of pyridine and sulfonic acid groups at 1552.8 and 1036.5 cm^{-1}, respectively. The ratio between both areas corresponds to the copolymer composition (1:1), which was corroborated by elemental analysis through the sulfur content.

Metal-ion-retention properties

It is well known that hard acids, which are small and hardly polarizable, display a higher affinity toward hard donor atoms such as O or N, whereas soft acids, being larger and more easily polarizable, have a greater affinity toward soft donor atoms.[26] Thus, d(II) is a soft acid, and Hg(II) is a hard acid.

Figure 2 shows the effect of the pH on the metal-ion retention for the cations Cu(II), Cd(II), Hg(II), Pb(II), Zn(II), and Cr(III) by the batch procedure equilibrium. The resin/metal-ion molar ratio studied was 20/1 so that a great excess of the ligand sites would be ensured. The initial amount of each metal ion was 0.16 mmol/g of dry resin. The results demonstrate that the resin has a great affinity for the mercury ions. The retention at pH 2.0 was 100%, whereas for the other metal ions it was lower than 55%.

According to these results, the other runs were carried out with the mercury ions as the central interest.

The kinetics of metal uptake were measured for the resin. Figure 3 shows that the resin removes the Hg(II) ions and that the uptake is fast, with 100% of the cations sorbed within 5 min.

To explore the applications of the resin, we needed to determine the sorption capacity of the resin toward Hg(II) ions, and so the maximum load retention of the P(APSA-*co*-4VPy) resin was determined at pH 2.0. The

Figure 6 Elution (mg) of Hg(II) from the P(APSA-*co*-4VPy) resin loaded at different concentrations.
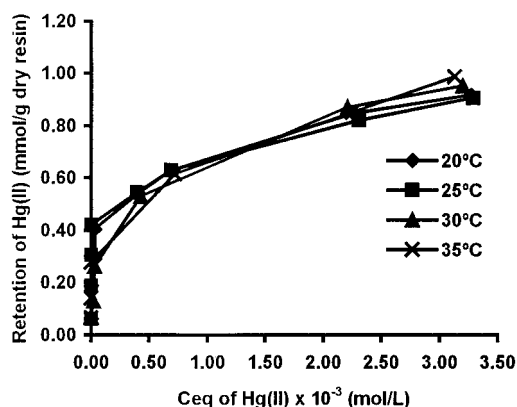
Figure 8 Retention [mmol of Hg(II) ions/g of resin] versus the initial amount of Hg(II) (mmol; column equilibrium procedure).
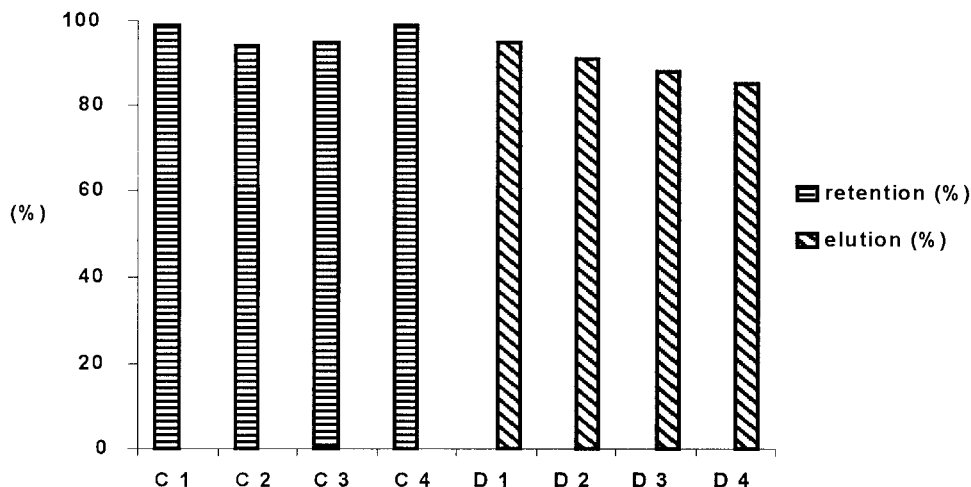
Figure 9 Sorption (*Cx*) and desorption (*Dy*) cycles (%) of Hg(II) for the P(APSA-*co*-4VPy) resin (batch equilibrium procedure).

value obtained was 83.5%, which corresponded to 0.23 mmol/g of dry resin.

To determine the metal-ion retention under competitive conditions, we mixed 50 mg of the resin at pH 2.0 for 1 h with a 5-mL aqueous solution containing the same concentration of each metal ion. The resin showed a high selectivity for Hg(II) (99.9%) with respect to the other metal ions [Cu(II), 0%; Cr(III), 0%; Zn(II), 0%; Pb(II), 4.3%; and Cd(II), 7.0%].

To be useful in the ion-recycling process, the metal ion adsorbed by the resin should be easily released under appropriate conditions. The batch desorption studies were carried out by the samples of the resin being loaded exclusively with Hg(II) followed by a treatment with an excess of the ex-

tracting reagent. Two extractants were chosen: $HClO_4$ and HNO_3. Both reagents act in a similar way. They are able to displace anionic metal complexes being ionically sorbed onto cationic functional groups. The results of the desorption are shown in Figure 4. With respect to the elution data, it is evident that the two eluent reagents behave similarly. This result supports the assumption that the retention of Hg(II) is caused not exclusively by ion pairing but also by a coordinative bonding between this metal and the complexing functionalities.

The capacity of the resin to remove Hg(II) ions was tested under dynamic conditions by a solution of Hg(II) at pH 2.0 being passed through a column. The packing of the column was carried out with 200 mg of
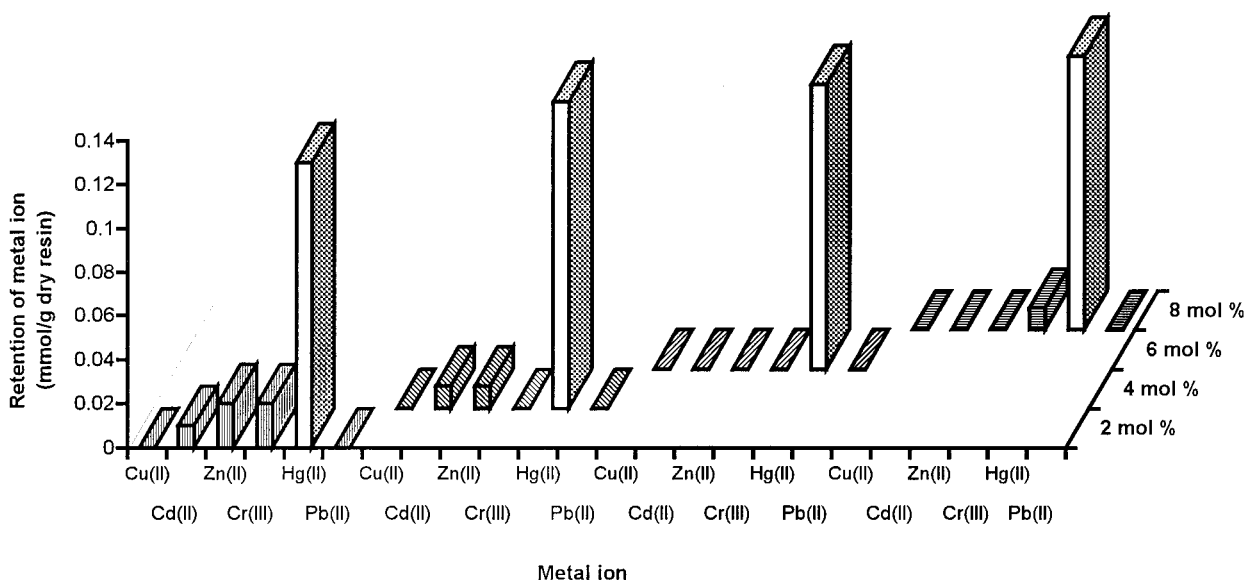
Figure 10 Metal-ion retention under competitive conditions (column equilibrium procedure).
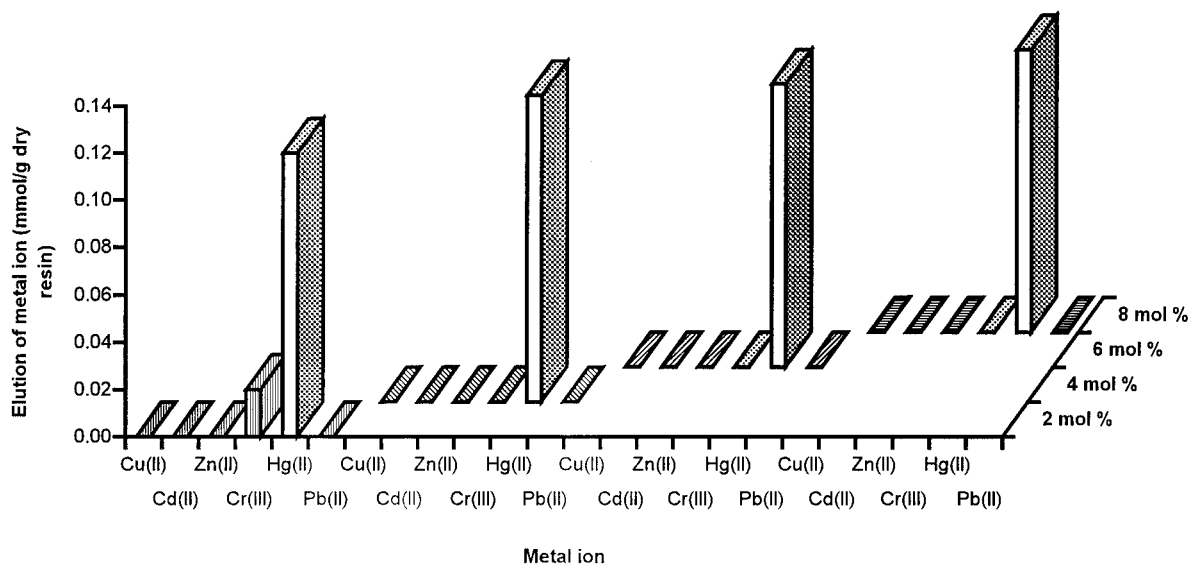
Figure 11 Metal-ion elution from the loaded resin under competitive conditions.

the resin at 20°C. The time of flux was 13 min. The results are given in the next figures.

Figure 5 shows the effect of the mercury-ion concentration on the retention with the column equilibrium procedure. The run was carried out with 50 mg of the dry resin and 5 mL of the mercury-ion solution for 13 min. The initial concentration varied between 0.05 and 0.005 mmol. The active sites were saturated rapidly because with 0.005 mmol, the mercury-ion retention was complete.

No important effect of the crosslinking degree and temperature on the mercury-ion retention was observed (see Figs. 6 and 7,) and the equilibrium was achieved very quickly in a way similar to that used for the batch procedure.

For all the experiments, the elution was greater than 90% with a treatment with $1M$ HClO$_4$ for 13 min (see Fig. 8). Moreover, the sorbent was able to withstand the strong acidic conditions, and its metal-ion-binding ability was retained after repeated acid treatments. Therefore, for resin reusability, the sorption–desorption cycle was repeated four times with the same sorbent. The initial amounts of Hg(II) were employed to load the resin. In each cycle, the desorption was carried out at pH 2 for 1 h. No important decrease in the metal-ion-retention affinity was found (see Fig. 9).

The retention of mercury ions was also investigated under competitive conditions through the column method. The aqueous metal-ion solution contained Cu(II), Cd(II), Zn(II), Pb(II), and Hg(II) at the same initial concentration (0.05 mmol). The results showed a very high selectivity for Hg(II) ions (see Fig. 10), which were quickly eluted with $4M$ HClO$_4$ (see Fig. 11).

CONCLUSIONS

Crosslinked P(APSA-co-4VPy), synthesized by solution radical polymerization, shows great promise for the removal of mercury ions from aqueous solutions, particularly at pH 2.0. The two most common equilibrium procedures, batch and column, were tested, and no important differences were found in the results. The Hg(II) ions were rapid, and the adsorption equilibrium was reached within 20 min. The adsorption capacity at pH 2.0 was 0.23 mmol/g of dry resin. No important effect of the crosslinking degree and temperature on the mercury-ion retention was observed. An elution of greater than 90% was obtained with 1–$4M$ HClO$_4$ and HNO$_3$. Consecutive adsorption and desorption showed the feasibility of this resin for Hg(II)-ion adsorption.

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